

PATENT ABSTRACTS OF JAPAN

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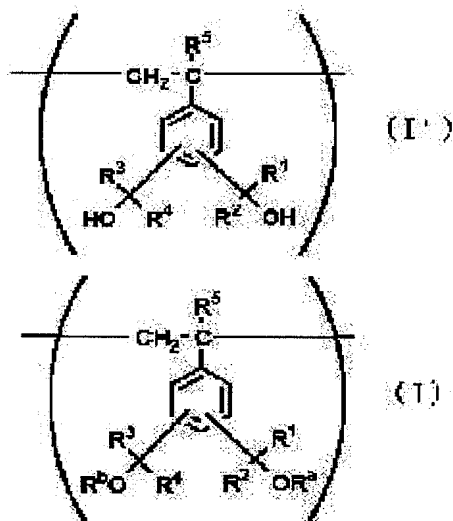
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(54) RESIST COMPOSITION



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resist composition excellent in transmittance to light of ≤ 170 nm wavelength and suitable particularly for F2 excimer laser lithography.

SOLUTION: The resist composition comprises a resin and an acid generator, wherein the resin undergoes a chemical change and becomes alkali-soluble by the action of the acid generator after irradiation with a radiation and contains a polymerized unit represented by formula (I') and a polymerized unit represented by formula (I). In the formula (I'), R1-R4 are each independently a 1-12C fluoroalkyl having at least one F atom and R5 is H, halogen,

cyano, a 1-3C alkyl or a 1-12C fluoroalkyl having at least one F atom. In the formula (I), R1-R4 have the same meanings as the above R1-R4 and Ra and Rb are each independently a group which is cleaved by an acid or H but at least one of Ra and Rb is a group which is cleaved by an acid.

LEGAL STATUS

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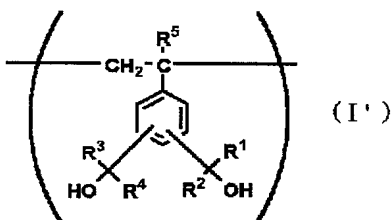
2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

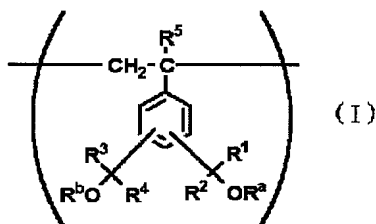
[Claim 1] The resist constituent characterized by containing resin and an acid generator, for this resin causing a chemical change by operation of the acid generator after radiation irradiation, serving as alkali fusibility, and including the polymerization unit shown by the bottom formula (I').



(R1, R2, R3, and R4 express among a formula the fluoro alkyl group of the carbon numbers 1-12 which have at least one fluorine atom independently, respectively, and R5 expresses a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or the fluoro alkyl group of the carbon numbers 1-12 which have at least one fluorine atom.)

[Claim 2] The constituent according to claim 1 each of whose R1, R2, R3, and R4 in said formula (I') is a trifluoromethyl radical.

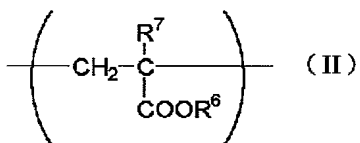
[Claim 3] The constituent according to claim 1 or 2 which is resin including the polymerization unit shown by the polymerization unit resin is indicated to be by said formula (I'), and the bottom formula (I).



(Among a formula, respectively independently [R1, R2 R3, and R4], independently, the thing in a formula (I') expresses the fluoro alkyl group of the carbon numbers 1-12 which have at least one fluorine atom, and expresses the fluoro alkyl group of the carbon numbers 1-12 in which R5 has a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or at least one fluorine atom.) Moreover, Ra and Rb express the radical or hydrogen atom which **** with an acid independently, respectively. However, at least one side of Ra and Rb expresses the radical which **** with an acid.

[Claim 4] The constituent according to claim 3 each of Ra in said formula (I) and whose Rb(s) is the radicals which cleave with an acid.

[Claim 5] A constituent including the polymerization unit shown by the polymerization unit resin is indicated to be by said formula (I'), and the bottom formula (II) according to claim 1 to 4.



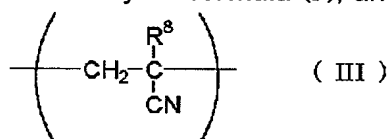
(R6 expresses among a formula the radical which **** in an operation of an acid, and R7 expresses a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or the fluoro alkyl group of the carbon numbers 1-3 which have at least one fluorine atom.)

[Claim 6] The constituent according to claim 5 whose R6 is a 2-alkyl-2-adamantyl radical in a formula (II).

[Claim 7] The constituent according to claim 5 or 6 whose R7 is a hydrogen atom, a methyl group, or a trifluoromethyl radical in a formula (II).

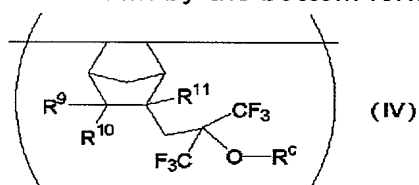
[Claim 8] The resin with which resin includes the polymerization unit shown by the polymerization unit shown by ** formula (I'), and the bottom formula (III), Or resin including the polymerization unit shown by the polymerization unit shown by the polymerization unit shown by ** formula (I'), and the formula (I), and the bottom

formula (III), Or the constituent according to claim 1 to 7 which is resin including the polymerization unit shown by the polymerization unit shown by the polymerization unit shown by ** formula (I'), and the formula (II), and the bottom formula (III).



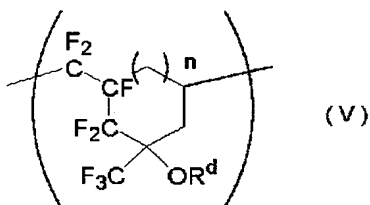
(R⁸ expresses among a formula a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or the fluoro alkyl group of the carbon numbers 1-3 which have at least one fluorine atom.)

[Claim 9] Furthermore, the constituent containing resin including the polymerization unit shown by the bottom formula (IV) according to claim 1 to 8.



(R⁹, R¹⁰, and R¹¹ express a hydrogen atom, a halogen atom, a hydroxyl group, the alkyl group of carbon numbers 1-14, an alicyclic ring, or a lactone ring independently among a formula, respectively.) This alkyl group may be permuted with the halogen atom, the hydroxyl group, or the alicyclic ring. The alicyclic ring and lactone ring which are R⁹, R¹⁰, or R¹¹ may be independently permuted by the halogen atom, the hydroxyl group, or the alkyl group, respectively. R^c expresses the radical which cleaves with an acid.

[Claim 10] Furthermore, the constituent containing resin including the polymerization unit shown by the bottom formula (V) according to claim 1 to 9.



(n shows the integer of 0-1 among a formula.) R^d expresses the radical which cleaves with an acid.

[Claim 11] The constituent according to claim 1 to 10 with which an acid generator is the activity compound which generates an acid according to an operation of a

radiation, and acts on a positive type.

[Claim 12] The constituent according to claim 1 to 11 which contains resin 60 to 99.9% of the weight, and contains an acid generator in 40 – 0.1% of the weight of the range to the sum total weight of resin and an acid generator.

[Claim 13] Furthermore, the constituent containing a basic compound according to claim 1 to 12.

[Claim 14] The constituent according to claim 1 to 13 whose basic compound is the range of 0.001 – 1 weight section to the resin 100 weight section.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resist constituent used for micro processing of a semi-conductor.

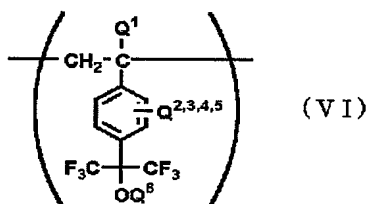
[0002]

[Description of the Prior Art] It is so possible that exposure wavelength is theoretically short so that the lithography process which used the resist constituent may usually be adopted as micro processing of a semi-conductor and it may be expressed with the formula of Rayleigh (Rayleigh) of a diffraction limitation in lithography to raise resolution. The exposure light source for lithography used for manufacture of a semi-conductor serves as g line with a wavelength of 436nm, i line with a wavelength of 365nm, a KrF excimer laser with a wavelength of 248nm, and an ArF excimer laser with a wavelength of 193nm to short wavelength every year, and promising ** of the F2 excimer laser with a wavelength of 157nm is further carried out as the next-generation exposure light source. Many so-called chemistry magnification mold resists using the catalysis of the acid generated by exposure are used for KrF excimer laser exposure or ArF excimer laser exposure from excelling in sensibility. And possibility that a chemistry magnification mold resist will be used for F2 excimer-laser exposure in respect of sensibility is high.

[0003] The resin of a polyvinyl phenol system has been used for the resist for KrF excimer laser exposure. On the other hand, in order for the resin used for the resist for ArF excimer laser exposure not to have a ring in order to secure the transmission of a resist, and to give dry etching resistance, it is known that what has an alicyclic ring instead of a ring is good.

[0004] However, the resin used for the resist the conventional KrF excimer laser exposure and for ArF excimer laser exposure did not show sufficient permeability to light with a wavelength of 170nm or less, for example, F2 excimer laser with a wavelength of 157nm. If permeability is low, it will have a bad influence on many engine performance, such as a profile, contrast, and sensibility.

[0005] Moreover, in the Germany JP,4207261,B specification, the polymer containing the following polymerization unit (VI) is examined as a positive resist.



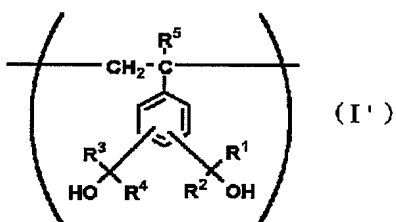
[(The aralkyl radical of the carbon numbers 7-20 which may be permuted with the aromatic series radical or halogen of carbon numbers 6-14 which may be permuted with the alkyl group of the carbon numbers 1-4 by which Q1 may be permuted with a hydrogen atom or a halogen, the aliphatic series radical of the carbon numbers 1-20 by which Q2-Q5 may be independently permuted with a hydrogen atom, a halogen atom, or a halogen, respectively, or a halogen, and Q6 express a ***** machine)
0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is excellent in the transmission to light with a wavelength of 170nm or less, and is to offer the resist constituent which fitted F2 excimer-laser lithography especially.

[0007]

[Means for Solving the Problem] this invention persons completed a header and this invention for the ability of amelioration of the permeability in the balance of the engine performance, and the wavelength of F2 157nm excimer laser to be performed by using the resin which has the polymerization unit which originates in a specific monomer as resin which constitutes a resist constituent.

[0008] That is, resin and an acid generator are contained, this resin causes a chemical change by operation of the acid generator after radiation irradiation, serves as alkali fusibility, and this invention relates to a resist constituent including the polymerization unit shown by the bottom formula (I').



(R1, R2, R3, and R4 express among a formula the fluoro alkyl group of the carbon numbers 1-12 which have at least one fluorine atom independently, respectively, and R5 expresses a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or the fluoro alkyl group of the carbon numbers 1-12 which have at least one fluorine atom.)

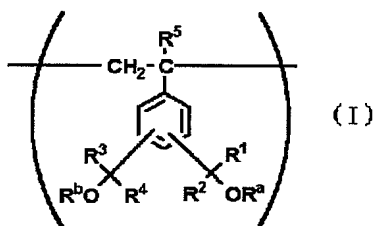
[0009]

[Embodiment of the Invention] In this invention, the radiation irradiation section of the resist film is removed by alkali development, and serves as a positive resist. That is, the positive resist of a chemistry magnification mold makes the radiation irradiation section meltable in an alkali water solution by carrying out regeneration of an acid or the base while the acid or base generated from the acid generator in the radiation irradiation section is spread by subsequent heat treatment (post exposure bake) and making it **** protective groups, such as resin.

[0010] In the resist constituent of this invention, the resin which has as resin the polymerization unit shown by the above-mentioned formula (I') is used. The resin in this invention may be called binder resin. That each of whose R1, R2, R3, and R4 in said formula (I') is a trifluoromethyl radical is desirable.

[0011] By incorporating the polymerization unit of a formula (I') into binder resin, this resin becomes the thing excellent in the permeability to light with a wavelength of 170nm or less, for example, F2 excimer laser with a wavelength of 157nm. What is necessary is just to choose after radiation irradiation as a rate including the polymerization unit expressed with a formula (I'), in the resin in this invention, in the range which becomes meltable in an alkali water solution according to an operation of an acid generator, although the ratio of arbitration can be chosen, and resin itself is insoluble or refractory to an alkali developer.

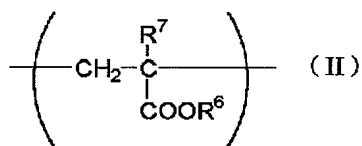
[0012] The constituent containing resin including the polymerization unit shown as a resist constituent of this invention by the polymerization unit resin is indicated to be by said formula (I'), and the bottom formula (I) is mentioned.



(Among a formula, respectively independently [R1, R2 R3, and R4], independently, the thing in a formula (I') expresses the fluoro alkyl group of the carbon numbers 1-12 which have at least one fluorine atom, and expresses the fluoro alkyl group of the carbon numbers 1-12 in which R5 has a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or at least one fluorine atom.) Moreover, Ra and Rb express the radical or hydrogen atom which **** with an acid independently, respectively. However, at least one side of Ra and Rb expresses the radical which **** with an acid. It is desirable that it is the radical which each of Ra and Rb(s) **** with an acid. When Ra in a formula (I) and Rb are the radicals which cleave with an acid, the radical which has dissolution suppression ability to an alkali developer is used. The resin which has the radical which cleaves with the acid mentioned above is preferably applicable as a positive resist which used the acid generator.

[0013] The radical which the 4th class carbon like tert-butyl, a tert-butoxycarbonyl radical, or a tert-butoxy carbonylmethyl radical combined with the oxygen atom as a radical which cleaves with this acid, for example; A tetrahydro-2-pyranyl radical, A tetrahydro-2-furil radical, a methoxymethyl radical, an ethoxymethyl radical, 1-adamanthyl oxymethyl radical, a t-butoxy methyl group, an i-propoxy methyl group, 1-ethoxyethyl radical, 1-(2-methyl propoxy) ethyl group, 2-methoxyethoxymethyl radical, 1-(2-methoxyethoxy) ethyl group, 1-(2-acetoxyethoxy) ethyl group, A 1-[2-(1-adamantyloxy) ethoxy] ethyl group or the radical of an acetal mold like a 1-[2-(1-adamantane carbonyloxy) ethoxy] ethyl group; A 3-oxocyclohexyl radical, The radical of a non-aromatic ring compound like a 4-methyl tetrahydro-2-pyrone-4-IRU radical (led from mevalonic lactone), a 1-adamanthyl-1-alkyl alkyl group, or a 2-alkyl-2-adamanthyl radical etc. is mentioned. These radicals may be named generically and it may be called the acid cleavage machine group A.

[0014] Furthermore, the constituent containing resin including the polymerization unit shown as a resist constituent of this invention by the polymerization unit shown by said formula (I') and the bottom formula (II) is mentioned.

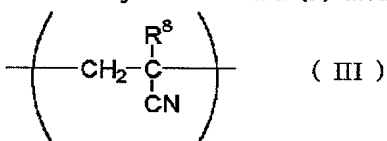


(R6 expresses among a formula the radical which **** in an operation of an acid, and R7 expresses a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or the fluoro alkyl group of the carbon numbers 1-3 which have at least one fluorine atom.)

[0015] In a formula (II), as R6, the aforementioned acid cleavage machine group A is mentioned, and a 2-alkyl-2-adamantyl radical is mentioned preferably.

[0016] In a formula (II), a hydrogen atom, a methyl group, or a trifluoromethyl radical is preferably mentioned as R7.

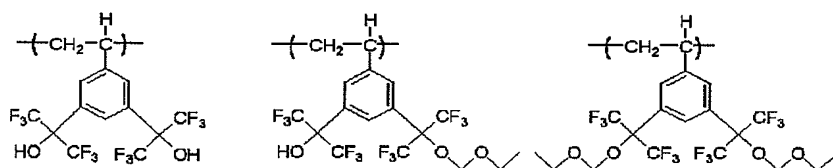
[0017] Furthermore, the resin with which resin includes the polymerization unit shown by the polymerization unit shown by ** formula (I'), and the bottom formula (III) as a constituent of this invention, Or resin including the polymerization unit shown by the polymerization unit shown by the polymerization unit shown by ** formula (I'), and the formula (I), and the bottom formula (III), Or the constituent which is resin including the polymerization unit shown by the polymerization unit shown by the polymerization unit shown by ** formula (I') and the formula (II) and the bottom formula (III) is mentioned.



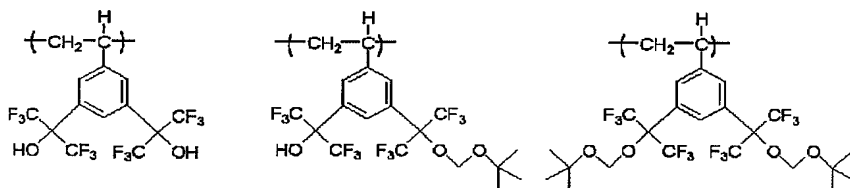
(R8 expresses among a formula a hydrogen atom, a halogen atom, a cyano group, the alkyl group of carbon numbers 1-3, or the fluoro alkyl group of the carbon numbers 1-3 which have at least one fluorine atom.)

[0018] One of the polymerization units shown by the formula (I') and the formula (I), the formula (II), and the formula (III) is incorporated, and if some typical examples are given about the binder resin which causes a chemical change by operation of the acid generator after radiation irradiation, and serves as fusibility at an alkali water solution, the resin which has a polymerization unit as shown below will be mentioned.

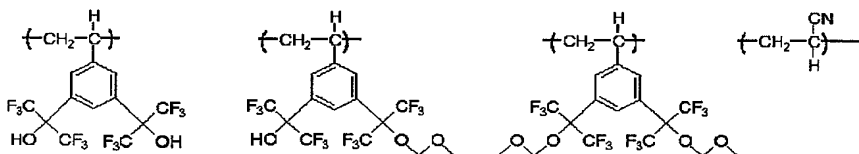
[0019] Resin which has the following polymerization unit (a)



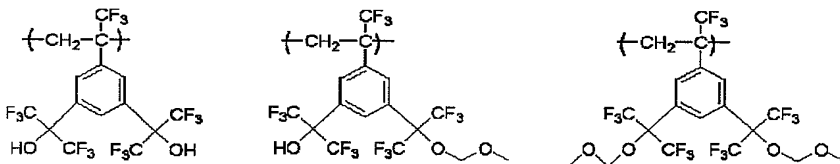
[0020] Resin which has the following polymerization unit (b)



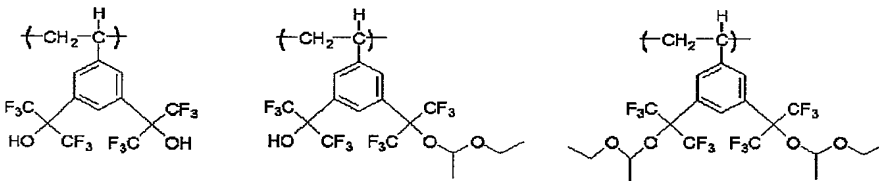
[0021] Resin which has the following polymerization unit (c)



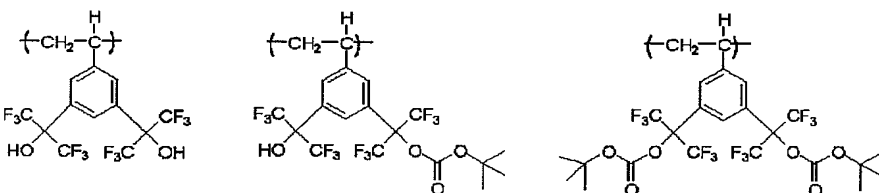
[0022] Resin which has the following polymerization unit (d)



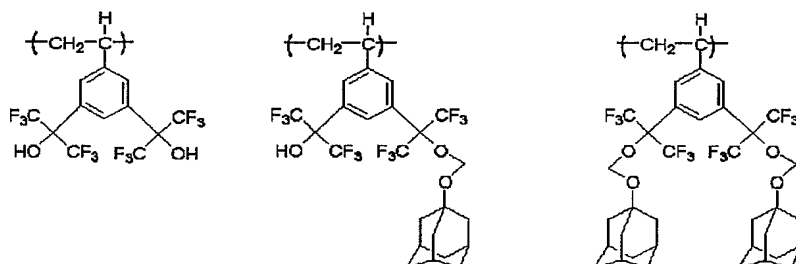
[0023] Resin which has the following polymerization unit (e)



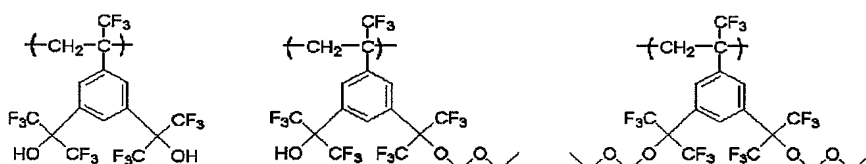
[0024] Resin which has the following polymerization unit (f)



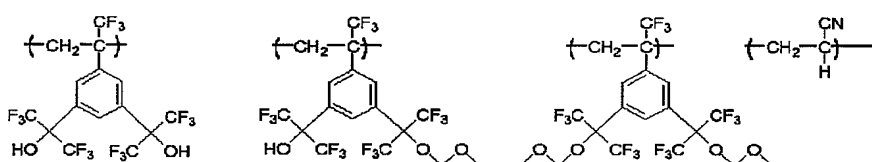
[0025] Resin which has the following polymerization unit (g)



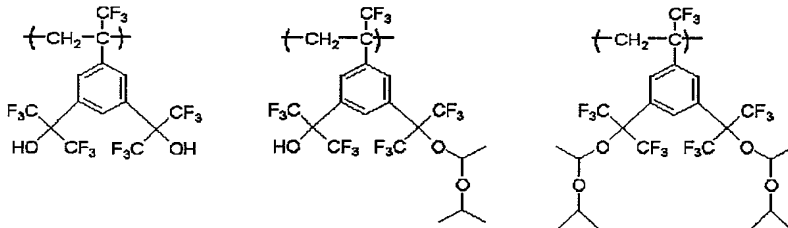
[0026] Resin which has the following polymerization unit (h)



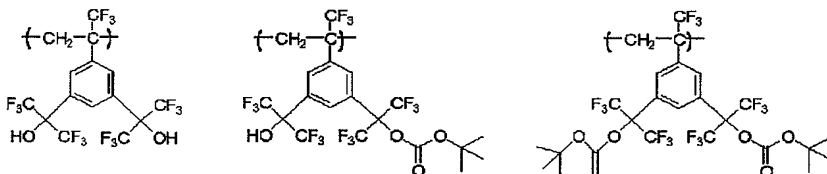
[0027] Resin which has the following polymerization unit (i)



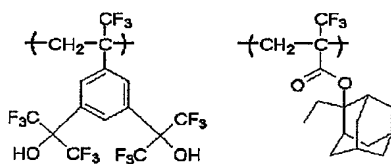
[0028] Resin which has the following polymerization unit (j)



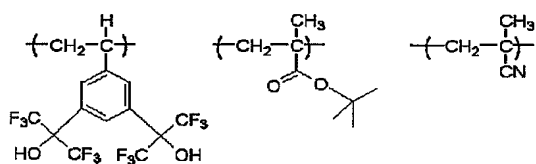
[0029] Resin which has the following polymerization unit (k)



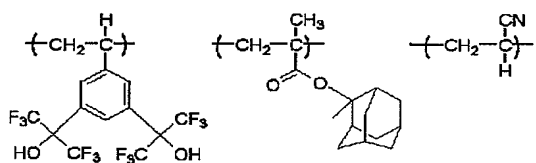
[0030] Resin which has the following polymerization unit (l)



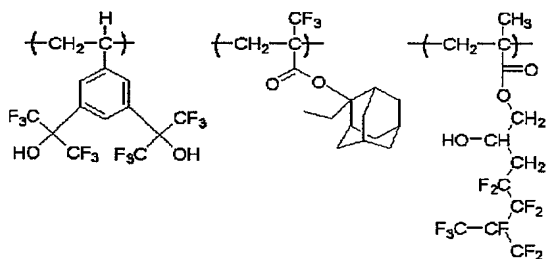
[0031] Resin which has the following polymerization unit (m)



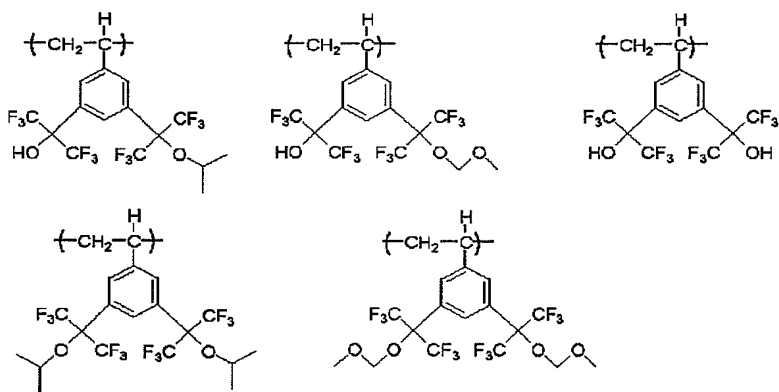
[0032] Resin which has the following polymerization unit (n)



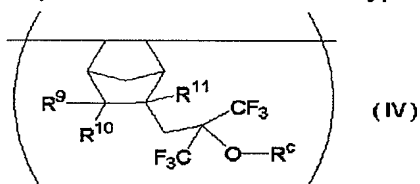
[0033] Resin which has the following polymerization unit (o)



[0034] Resin which has the following polymerization unit (p)



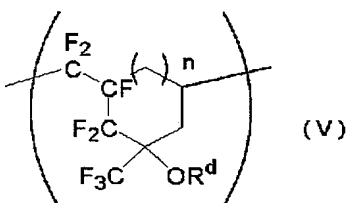
[0035] The resin in this invention can be used mixing with the binder resin of further others. The fluorine content norbornene polymer which has the polymerization unit expressed with a bottom type (IV) as this binder resin is mentioned.



(R9, R10, and R11 express a hydrogen atom, a halogen atom, a hydroxyl group, the alkyl group of carbon numbers 1–14, an alicyclic ring, or a lactone ring independently among a formula, respectively.) This alkyl group may be permuted with the halogen atom, the hydroxyl group, or the alicyclic ring. The alicyclic ring and lactone ring which are R9, R10, or R11 may be independently permuted by the halogen atom, the hydroxyl group, or the alkyl group, respectively. Rc expresses the radical which cleaves with an acid.

[0036] As Rc in a formula (IV), the radical of the aforementioned ***** machine A group is mentioned.

[0037] As other binder resin which can carry out mixed use, the polymer containing a fluorine is also mentioned to the principal chain expressed with a bottom type (V).



(n shows the integer of 0–1 among a formula.) Rd expresses the radical which cleaves with an acid.

[0038] As Rd in a formula (V), the radical of the aforementioned ***** machine A group is mentioned.

[0039] The resist constituent of this invention contains further the acid generator decomposed according to an operation of a radiation by using as binder resin the resin which can serve as the above alkali fusibility. as an acid generator — the matter itself — or various kinds of compounds which generate an acid are mentioned to the resist constituent containing the matter by irradiating a radiation. For example, onium salt, alkyl halide triazine compound, a disulfon system compound, the compound that has a diazomethane sulfonyl frame, a sulfonate system compound, etc. are mentioned. The

example of such an acid generator is shown below.

[0040] Onium salt: Diphenyliodonium Trifluoromethane sulfonate, 4-methoxyphenyl phenyliodonium Hexafluoroantimonate, 4-methoxyphenyl phenyliodonium Trifluoromethane sulfonate, Bis(4-tert-buthylphenyl) iodonium Tetrafluoroborate, Bis(4-tert-buthylphenyl) iodonium Hexafluorophosphate, Bis(4-tert-buthylphenyl) iodonium Hexafluoroantimonate, Bis(4-tert-buthylphenyl) iodonium Trifluoromethane sulfonate, a screw (4-t-buthylphenyl iodonium camphor sulfonate --) Triphenylsulfonium Hexafluorophosphate, triphenylsulfonium Hexafluoroantimonate, Triphenylsulfonium Trifluoromethane sulfonate, 4-methoxyphenyl diphenyl sulfonium Hexafluoroantimonate, 4-methoxyphenyl diphenyl sulfonium Trifluoromethane sulfonate, p-tolyl diphenyl sulfonium Trifluoromethane sulfonate, 2, 4, 6-trimethyl phenyl diphenyl sulfonium Trifluoromethane sulfonate, 4-tert-buthylphenyl diphenyl sulfonium Trifluoromethane sulfonate, 4-phenylthiophenyl diphenyl sulfonium Hexafluorophosphate, 4-phenylthiophenyl diphenyl sulfonium Hexafluoroantimonate, 1-(2-naphtoylmethyl)thiolanium Hexafluoroantimonate, 1-(2-naphtoylmethyl)thiolanium Trifluoromethane sulfonate, 4-hydroxy-1-naphthyl dimethyl sulfonium Hexafluoroantimonate, 4-hydroxy-1-naphthyl dimethyl sulfonium Trifluoromethane sulfonate etc.

[0041] Alkyl halide triazine compound : The 2-methyl -4, 6-bis(trichloromethyl)-1,3,5-triazine, 2, 4, 6-tris (trichloromethyl)-1,3,5-triazine, The 2-phenyl -4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-chlorophenyl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxy-1-naphthyl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-([Benzod] [1, 3] dioxolane-5-IRU)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(3, 4, 5-trimethoxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(3, 4-dimethoxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(2, 4-dimethoxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(2-methoxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-butoxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-pentyloxy styryl)-4, 6-bis(trichloromethyl)-1,3,5-triazine, etc.

[0042] Disulfon system compound: Diphenyl Disulfon, G p-tolyl Disulfon, phenyl p-tolyl Disulfon, phenyl p-methoxyphenyl Disulfon etc.

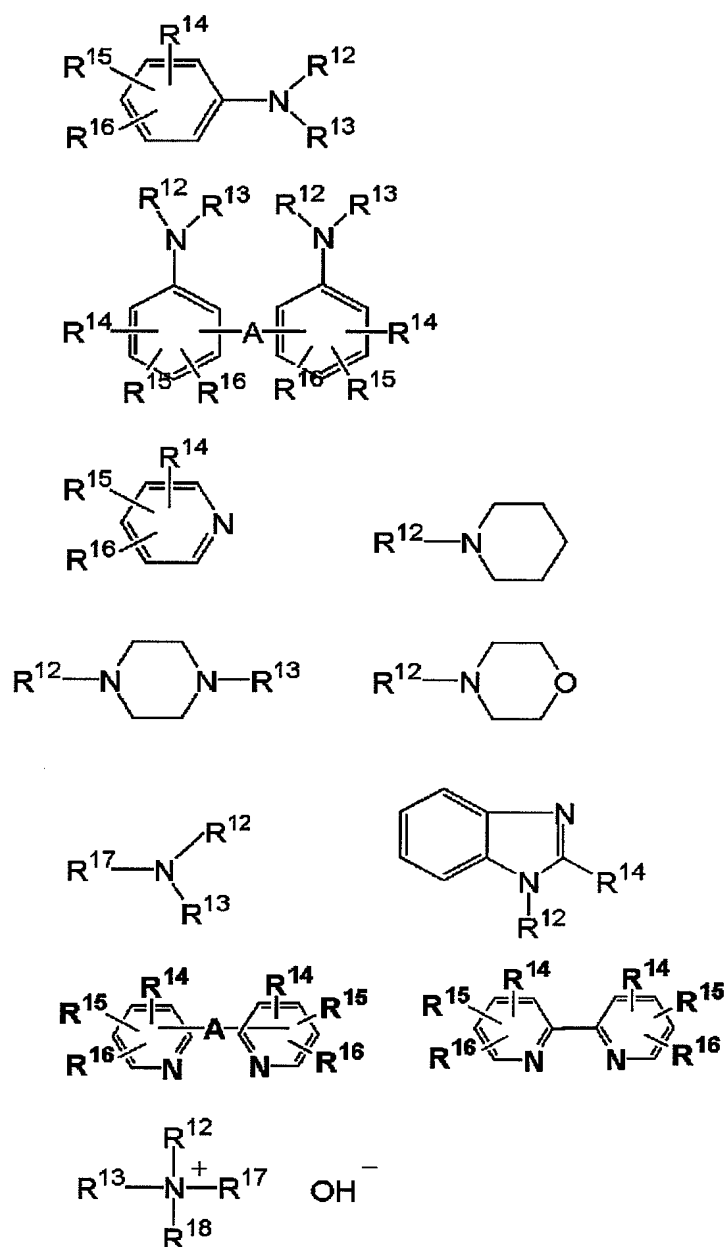
[0043] The compound which has a diazomethane sulfonyl frame: Bis(phenyl sulfonyl) diazomethane, bis(4-chlorophenyl sulfonyl) diazomethane, bis(p-tolyl sulfonyl)

diazomethane, bis(4-tert-buthylphenyl sulfonyl) diazomethane, bis(2, 4-xylyl sulfonyl) diazomethane, bis(cyclohexyl sulfonyl) diazomethane, diazomethane (phenyl (benzoyl) sulfonyl), etc.

[0044] Sulfonate system compound: 1-benzoyl-1-phenylmethyl P-toluene sulfonate (common-name benzoin tosylate), 2-benzoyl-2-hydroxy-2-phenylethyl P-toluene sulfonate (common-name alpha-methylol benzoin tosylate), 1, 2, 3-benzene Trier Tris methanesulfonate, 2, 6-dinitro benzyl P-toluene sulfonate, 2-nitrobenzyl P-toluene sulfonate, 4-nitrobenzyl P-toluene sulfonate, N-(phenylsulfonyloxy)succinimide, N-(p-tolyl sulfonyloxy) succinimide, N-(trifluoromethyl sulfonyloxy)succinimide, an N-(isopropyl sulfonyloxy) succinimide N-(n-butyl sulfonyloxy) succinimide, N-(n-hexyl sulfonyloxy) succinimide, N-(10-camphor sulfonyloxy) succinimide, N-(trifluoromethyl sulfonyloxy)phthalimide, N-(trifluoromethyl sulfonyloxy)-5-norbornene -2, 3-dicarboxyimide, N-(trifluoromethyl sulfonyloxy)naphthalimide, N-(10-camphor sulfonyloxy) North America Free Trade Agreement RUIMIDO, etc.

[0045] In the constituent of this invention, the performance degradation by deactivation of the acid by which it is accompanied every length after exposure is improvable by adding an organic base compound, especially a nitrogen-containing basicity organic compound. This organic base compound may be called a quencher to below. As a concrete example of such a nitrogen-containing basicity organic compound, the amines shown by each following formula can be mentioned.

[0046]



[0047] R^{12} , R^{13} , and R^{18} express hydrogen, alkyl, cycloalkyl, or aryl independently among a formula, respectively. This alkyl, cycloalkyl, or aryl may be independently permuted by the hydroxyl group, the amino group, or the alkoxy group of carbon numbers 1–6, respectively. This amino group may be permuted by the alkyl group of carbon numbers 1–4. Moreover, this alkyl has about one to six desirable carbon number, this cycloalkyl has about five to ten desirable carbon number, and this aryl has about six to ten desirable carbon number. R^{14} , R^{15} , and R^{16} express hydrogen,

alkyl, cycloalkyl, aryl, or ARUKOKISHI independently, respectively. this alkyl, cycloalkyl, aryl, or alkoxy ** -- respectively -- independent -- a hydroxyl group, the amino group, or the alkoxy group of carbon numbers 1-6 -- you may come out and permute. This amino group may be permuted by the alkyl group of carbon numbers 1-4. Moreover, this alkyl has about one to six desirable carbon number, this cycloalkyl has about five to ten desirable carbon number, this aryl has about six to ten desirable carbon number, and this alkoxy ** and its about one to six carbon number are desirable. R17 expresses alkyl or cycloalkyl. this alkyl or cycloalkyl -- respectively -- independent -- a hydroxyl group, the amino group, and the alkoxy group of carbon numbers 1-6 -- you may come out and permute. This amino group may be permuted by the alkyl group of carbon numbers 1-4. Moreover, this alkyl has about one to six desirable carbon number, and this cycloalkyl has about five to ten desirable carbon number. A expresses alkylene, carbonyl, an imino ** sulfide, or disulfide. As for this alkylene, it is desirable that it is about two to six carbon number. Moreover, in R12-R18, the any are sufficient about what can take both straight chain structure and branching structure. [0048] As such a compound, specifically Hexylamine, a heptyl amine, An octyl amine, a nonyl amine, a DESHIRU amine, an aniline, 2-, 3-, or 4-methylaniline, 4-nitroaniline, 1- or 2-naphthylamine, ethylenediamine, The tetramethylenediamine, hexamethylenediamine, 4, and 4'-diamino -1, 2-bibenzyl, The 4 and 4'-diamino -3, 3'-dimethyl diphenylmethane, 4, and 4'-diamino -3, 3'-diethyl diphenylmethane, Dibutyl amine, dipentylamine, a dihexyl amine, diheptylamine, A dioctyl amine, a dinonyl amine, a JIDESHIRU amine, N-methylaniline, A piperidine, a diphenylamine, triethylamine, a trimethylamine, Tripropylamine, tributylamine, tripentylamine, trihexyl amine, A triheptyl amine, trioctylamine, a TORINO nil amine, a tridecyl amine, Methyl dibutyl amine, methyl dipentylamine, a methyl dihexyl amine, Methyl dicyclohexylamine, methyl diheptylamine, a methyl dioctyl amine, A methyl dinonyl amine, a methyl JIDESHIRU amine, ethyl dibutyl amine, Ethyl dipentylamine, an ethyl dihexyl amine, ethyl diheptylamine, An ethyl dioctyl amine, an ethyl dinonyl amine, an ethyl JIDESHIRU amine, Dicyclohexyl monomethylamine, a tris [2-(2-methoxyethoxy) ethyl] amine, Tri-isopropanolamine, N.N-dimethylaniline, 2, 6-isopropyl aniline, An imidazole, a pyridine, 4-methylpyridine, 4-methyl imidazole, A bipyridine, 2, and 2'-dipyridyl amine, a G 2-pyridyl ketone, 1, 2-JI (2-pyridyl) ethane, 1, 2-JI (4-pyridyl) ethane, 1, 3-JI (4-pyridyl) propane, 1, 2-bis(2-pyridyl) ethylene, 1, 2-bis(4-pyridyl) ethylene, 1, 2-bis(4-pyridyloxy) ethane, 4 and 4'-dipyridyl sulfide, 4, and 4'-dipyridyl disulfide, 1, 2-bis(4-pyridyl) ethylene, 2, and 2'-dipicolylamine, 3 and 3'-dipicolylamine, tetramethylammonium hydroxide, Tetra-isopropyl ammonium hydroxide,

tetrabutylammonium hydroxide, Tetra--n-hexyl ammonium hydroxide, tetra--n-octyl ammonium hydroxide, Phenyltrimethylammonium hydroxide, 3-(trifluoromethyl) phenyltrimethylammonium hydroxide, a choline, etc. can be mentioned.

[0049] Furthermore, the hindered amine compound which has a piperidine frame which is indicated by JP,11-52575,A can also be used.

[0050] As for the resist constituent of this invention, it is still more desirable that it is desirable that contain resin and it contains an acid generator in 40 – 0.1% of the weight of the range 60 to 99.9% of the weight to the sum total weight of resin and an acid generator, and contain binder resin and it contains an acid generator in 20 – 0.1% of the weight of the range 80 to 99.9% of the weight.

[0051] Moreover, in the constituent of this invention, when using a basic compound, it is desirable to contain in the range of 0.01 – 1 weight section extent to the binder resin 100 weight section. Furthermore, the constituent of this invention can also carry out little content of various kinds of additives, such as a sensitizer, other resin, a surfactant, a stabilizer, and a color, if needed.

[0052] Each above-mentioned component usually serves as a resist constituent of a liquid in the condition of having dissolved in the solvent, and the resist constituent of this invention is applied on bases, such as a silicon wafer, according to conventional methods, such as spin coating. The solvent used here dissolves each component and has a suitable rate of drying, and after a solvent evaporates, the solvent generally used in this field can use it that what is necessary is just what gives a uniform and smooth paint film.

[0053] For example, the ester like ether; ethyl lactate like glycol-ether-ester; diethylene-glycol wood ether like ethylcellosolve acetate, methyl-cellosolve acetate, or propylene-glycol-monomethyl-ether acetate, butyl acetate, amyl acetate, or pyruvic-acid ethyl; the cyclic ester like ketones; or gamma-butyrolactone like an acetone, methyl isobutyl ketone, 2-heptanone, or a cyclohexanone can be mentioned. These solvents are independent, respectively, or can be combined two or more sorts and can be used.

[0054] It is applied on a base, and exposure processing for patterning is performed, and after performing heat-treatment for subsequently promoting a deprotection radical reaction or crosslinking reaction, negatives are developed by the dried resist film with an alkali developer. Although the alkali developers used here can be various kinds of alkaline water solutions used in this field, generally the water solution of tetramethylammonium hydroxide or trimethylammonium (2-hydroxyethyl) hydroxide (common-name choline) is used in many cases. In the above, although the gestalt of

operation of this invention was explained, the gestalt of operation of this invention indicated above is instantiation to the last, and the range of this invention is not limited to the gestalt of these operations. The range of this invention is shown by the claim and includes all modification in the publication of a claim, equal semantics, and within the limits further.

[0055]

[Example] Next, although an example is given and this invention is explained still more concretely, this invention is not limited at all by these examples. The section in an example is weight criteria as long as there is no special mention. Moreover, weight average molecular weight is the value calculated by the gel permeation chromatography by using polystyrene as a reference standard.

[0056] (1a) 3 and 5-bis(2-hydroxy hexafluoro isopropyl) styrene 2.25g and methyl-isobutyl-ketone 2.25g were taught to 50mL three-neck flask equipped with 3, the synthetic MAG stirring child of a 5-bis(2-hydroxy hexafluoro isopropyl) styrene polymer, a cooling pipe, a thermometer, and nitrogen installation tubing, the temperature up was carried out to 75 degrees C, and the solution in which 2.25g methyl isobutyl ketone was made to dissolve azobisisobutyronitril 0.025g was added. Then, it was kept warm for 10 hours and the resin which filled N-heptane 67.5g with reaction mixture, and deposited in it after cooling to the room temperature was taken out by the decantation. The amount of the obtained resin was 1.45g, the weight average molecular weight was 10901, and distribution was 1.7. This resin is set to A.

[0057] (1b) Resin A 0.8g, methyl-isobutyl-ketone 8.0g, and diisopropyl ethylamine 0.33g were taught to 50mL three-neck flask equipped with the formation 3 of partial ethoxymethyl, the synthetic MAG stirring child of a 5-bis(2-hydroxy hexafluoro isopropyl) styrene polymer, a cooling pipe, a thermometer, and nitrogen installation tubing, and 0.12g of ethoxymethyl chloride was added to it. Methyl isobutyl ketone was added after 4-hour churning at the room temperature, and ion exchange water washed the oil reservoir 8 times. It poured into [after condensing the obtained oil reservoir] the normal heptane, and depositing resin was taken out by the decantation. Then, reduced pressure drying was performed and resin was obtained. The amount of the obtained resin was 0.77g, the weight average molecular weight was 11805, and distribution was 1.6. Moreover, ethoxymethyl-ization was 29% to all hydroxyl groups. This resin is set to B.

[0058] (2a) Resin as well as the synthetic resin A of a 3 and 5-bis(2-hydroxy hexafluoro isopropyl) styrene polymer was obtained. The amount of the obtained resin was 1.56g, the weight average molecular weight was 9798, and distribution was 1.7.

This resin is set to C.

[0059] (2b) Resin A 0.8g, methyl-isobutyl-ketone 8.0g, and diisopropyl ethylamine 0.66g were taught to 50mL three-neck flask equipped with the formation 3 of partial ethoxymethyl, the synthetic MAG stirring child of a 5-bis(2-hydroxy hexafluoro isopropyl) styrene polymer, a cooling pipe, a thermometer, and nitrogen installation tubing, and 0.18g of ethoxymethyl chloride was added to it. At the room temperature, after 3-hour churning, further, 0.03g of ethoxymethyl chloride was added and it was agitated for 2 hours. Then, methyl isobutyl ketone was added and ion exchange water washed the oil reservoir 8 times. It poured into [after condensing the obtained oil reservoir] the normal heptane, and depositing resin was taken out by the decantation. Then, reduced pressure drying was performed and resin was obtained. The amount of the obtained resin was 0.34g and ethoxymethyl-ization was 45% to all hydroxyl groups. This resin is set to D.

[0060] The resist constituent was prepared using the acid generator and quencher which are shown in the following besides the resin B obtained like an example 1, next a synthetic example, and permeability was measured. Resist preparation mixed each following component, dissolved, was further filtered with the filter made of a fluororesin of 0.2 micrometers of apertures, and was performed.

[0061]

Resin B: 10 section acid generator: p-tolyl diphenyl sulfonium Perfluoro octane sulfonate 0.2 section quencher: Tetrabutylammonium hydroxide 0.0075 section solvent: Propylene-glycol-monomethyl-ether acetate The 95 sections The gamma-butyrolactone 5 section [0062] On the other hand, it applies so that the thickness after drying the prepared resist liquid as mentioned above may be set to 0.1 micrometers, and it prebaked to the magnesium fluoride wafer on the direct hot plate, and the resist film was made to form in it on 110-degree-C conditions for 60 seconds. In this way, it was 62% when the permeability in the wavelength of 157nm of the formed resist film was measured using the vacuum-ultraviolet spectrophotometer (Jasco Corp. Make).

[0063] Moreover, it was 65%, when the resin film was made to form and the permeability in 157nm was measured using the vacuum-ultraviolet spectrophotometer (Jasco Corp. Make) not about a resist presentation but about the solution made to dissolve Resin A in a solvent.

[0064] It was 46%, when compounded the example of comparison 14-(2-hydroxy hexafluoro isopropyl) styrene polymer, the resin film was made to form about the solution dissolved in the solvent and the permeability in 157nm was measured using

the vacuum-ultraviolet spectrophotometer (Jasco Corp. Make).

[0065]

[Effect of the Invention] In the exposure which used the light source with a wavelength of 170nm or less, for example, F2 excimer laser with a wavelength of 157nm, the resist constituent of this invention shows high transmission, and can demonstrate the outstanding engine performance as a resist constituent using the light source with a wavelength of 170nm or less.

[Translation done.]